PATENT ABSTRACTS OF JAPAN

(11)Publication number : **06-267593**
(43)Date of publication of application : **22.09.1994**

(51)Int.Cl. **H01M 10/52**

(21)Application number : **05-081255**
(22)Date of filing : **15.03.1993**

(71)Applicant : **YUASA CORP**
(72)Inventor : **IDO SHUICHI**
INAMASU TOKUO
TAKEDA KAZUNARI
YOSHIHISA HIROYOSHI

(54) **CELL**

(57)Abstract:
PURPOSE: To obtain a cell high in long term reliabilityand also high in safety by letting the cell contain material capable of absorbing gas generated within the celland of reacting on the aforesaid gas.
CONSTITUTION: Let gas absorbing agents corresponding to the kinds of gas generated be contained in a composite positive electrode 2a composite negative electrode 4a separator 3 and the like. In the case of hydrogen gaspalladiumpalladium treated carbon and the like exhibit excellent absorbing capacity. Besidesactivated carbon zeolitehollow glass microspheresorganic material such as ethyl ether and the like or metals absorbing hydrogen may be used. By this constitutionthe small size light sheet shaped cell can be obtainedwhich is high in long term reliabilityhigh in performanceand has high energy density.

CLAIMS

[Claim(s)]
[Claim 1]A compound anode (A) and a compound negative electrode (B_1)or a negative electrode (B_2) which comprises an electroactive substance.
The separator C.
It is the cell provided with the above and absorption or this gasand reactant are included for gas emitted within this cell in this cell.

[Claim 2]The cell according to claim 1wherein absorption or gasand reactant are contained on the compound anode (A) surface in a compound anode (A) in gas.
[Claim 3]The cell according to claim 1wherein absorption or gasand reactant are contained in gas on the inside of a compound negative electrode (B_1)the compound negative-electrode (B_1) surfaceor the surface of a negative electrode (B_2).

[Claim 4]The cell according to claim 1wherein absorption or gasand reactant are contained in a separator (C) in gas.
[Claim 5]The cell according to claim 1 by which absorption or gasand reactant being included for gas in cells other than an electrode and a separator.
[Claim 6]Absorption or gasand reactant gas The inside of a compound anode (A)the compound anode (A) surfaceThe cell according to claim 1 containing or more in two of the sorts in cells in the inside of a compound negative electrode (B_1)the compound negative-electrode (B_1) surface or the surface of a negative electrode (B_2)and a separator (C)or other than an electrode and a separator.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to improvement of the cell which operates reversibly under ambient air temperature.
[0002]
[Description of the Prior Art]The latest microelectronics-ization so that it may be represented by the power supply for memory backup of various electronic equipmentThe miniaturization of a cella weight savingslimming downand the cell that has high energy density further are strongly demanded with the unification with the storage in electronic equipment of a cellan electronics elementand a circuit. Thenas an electrode active materialit inquires especially about the thing using the intercalation or doping phenomenon of the laminar compoundand the charge-and-discharge cycle performance which was extremely excellent in these is expected.
[0003]The example of using a carbonaceous material as an electrode active material also appears as solution of problemssuch as the cycle characteristic of an electrode active material. Dope capacity with the high feature of this carbonaceous materialthe low rate of self-dischargethe outstanding cycle characteristicand the thing that should be mentioned most especially are having the less noble potential very near metal lithium. The cell which used the metallic oxide for the anode and generally used the lithium metalthe lithium alloyor the carbonaceous material for the negative electrode as a cell of this invention is mentioned.
[0004]
[Problem(s) to be Solved by the Invention]It is that a reaction occurs as a problem of the cell of this invention between the substances which constitute a celland gas is emitted. When especially a negative electrode is a lithium metalit is largea reactionsuch as drawing out hydrogenoccurs from the compound containing hydrogenand the reactivity generates hydrogen gas. The emitted gas has a problem which forms gas reservoir in bulging and the active material surface of a celland serves as a resistance tunic. For this reasonit was very lacking in long term reliability.
[0005]
[Means for Solving the Problem]A cellwherein this invention contains absorption or gasand reactant for gas characterized by comprising the following emitted within a cell in a cell.

A compound anode (A) and a compound negative electrode (B_1)or a negative electrode (B_2) which comprises a electron conductive substance arbitrarily with an electroactive substance that the above-mentioned purpose should be attained.
Separator (C).

[0006]Furthermoregas. Absorption. Gas and reactant Or inside of a compound anode (A). . Or are contained on the compound anode (A) surface. Or a thing which it is contained on the inside of a compound negative electrode (B_1)the compound negative-electrode (B_1) surfaceor the surface of a negative electrode (B_2)or it is contained in a separator (C)is contained in cells other than an electrode and a separatoror is included among four places above at two or more places. It is a cell by which it is characterized.
[0007]Although a gas absorbent in particular used for this invention is not limitedit needs to be cautious of changing with gas emitted. Especially in the case of hydrogen gasthe following show good absorption power. Although there are palladiumpalladium processing carbonpalladium processing MmO_2 platinum blackplatinumcarbon that carried out platinum processingmisch metals (example: MmNiFlAlCo (3.7:0.3:0.3:0.7) etc.)$LaNi_5$etc.it is not limited to these. Although absorptance is otherwise lowthere are organic matterssuch as activated carbon zeolitea hollow glass very small ball or ethyl etheracetonegelatinstarchand dextrin. As metal which absorbs hydrogenespecially although almost all things have the capabilityan element of V and III fellows is excellent.
[0008]It is also possible to add hydrogen to a reactant double bond by a method of fixing by a reaction. In this casein order to make an element of a group VIIIfor examplePcl etc.into a catalystit is necessary to include a catalyst in a cell with a compound including a reactant double bond.
[0009]Although a cell of this invention is an organic electrolysis liquid cell generally represented by a lithium cell or lithium ion batteryion-conductive polymers can also be used for a binder or a separator of a composite electrode.
[0010]With ion-conductive polymersalthough an ionic compound is made to contain in a polymers matrixplasticizerssuch as an organic solvent which can dissolve an ionic compound in otherscan also be included. Although what kind of polymer material it may generally be sufficient as a polymers matrixwhat has an ether group is typical.
[0011]As an ionic compoundfor example $LiClO_4$LiBF$_4$LiAsF$_6$LiPF$_6$LiCF$_3$SO$_3$LiCF$_3$CO$_2$LiSCNLiBrLiI$Li_2B_{10}Cl_{10}$$NaClO_4$NaINaSCNNaBrKClO$_4$Li(s)such as KSCNNaor an inorganic ion salt containing one sort of $K(CH_3)_4NBF_4$ and $_{(CH3)4}$NBr(C_2H_5) $_4$NClO$_4$ and $_{(C2H5)4}$NI(C_3H_7) $_4$NBr$_{(n\text{-}C4H9)\ 4}$NClO$_4$(n-C_4H_9) $_4$NI$_{(C2H5)4}$N-maleate(C_2H_5) Organic ion saltssuch as quarternary ammonium saltsuch as $_4$N-benzoate and $_{(C2H5)4}$N-phtalatestearylsulfonic acid lithiumoctylsulfonic acid lithiumand lithium dodecylbenzenesulfonateare mentioned. These ionic compounds may use two or more sorts together.
[0012]As a substance which can dissolve the above-mentioned ionic compoundCyclic estersuch as cyclic carbonate; gamma-butyrolactonesuch as propylene carbonate and ethylene carbonate; A tetrahydrofuran or its derivativeA nitril; dioxa run of ether; acetonitrilesuch as 13-dioxane12-dimethoxyethaneand methyldi glymebenzonitrileetc.or its derivative; sulfolane or its derivative is independentor these two or more sorts of mixtures etc. are mentioned. Howeverit is not limited to these. The blending ratio and a combination method are arbitrary. What a separator (C) becomes from a micropore film

or an ion-conductive high molecular compound of a polyolefin system is used.
[0013]A separator (C) which consists of an ion-conductive high molecular compoundIt is also possible to make the above-mentioned ion-conductive high molecular compound into a sheet shaped independentlyto arrange between the above-mentioned compound anode and a compound negative electrodeor to apply and harden the above-mentioned ion-conductive high molecular compound presentation liquid on a compound positive electrode surface or a compound negative electrode surfaceand to form a sheet-shaped cell.
[0014]About a coating method of the above-mentioned ion-conductive high molecular compound. For examplealthough it is desirable to apply to arbitrary thickness and arbitrary shape using meanssuch as roller coatingsuch as an applicator rollscreen coatinga doctor blade methodspin coatingand a bar coderit is not limited to these.
[0015]As positive active material used for a compound anode (A) of this inventionthe following charges of a battery electrode material are mentioned.
[0016]NamelyI group metal compoundssuch as $CuOCu_2OAg_2OCu$and $CuSO_4$Group IV metallic compoundssuch as $TiS_2SiO_2$and $SnOV_2O_5V_6O_{12}VOxNb_2O_5Bi_2O_3$Group-V-metals compoundssuch as $Sb_2O_3CrO_3Cr_2O_3VI$ group metallic compoundssuch as $MoO_3MoS_2WO_3$and SeO_2VII group metal compoundssuch as MnO_2 and $Mn_2O_3Fe_2O_3$Group VIII metal compoundssuch as $FeOFe_3O_4$nickel$_2O_3$NiOCo$O_3$and CoOor general formula Lix MX_2 and LixMNy X_2 (M.) N shows metal of a group VIII from Iand X shows charcogen compoundssuch as oxygen and sulfur. etc. -- it is expressed. For examplemetallic compoundssuch as a lithium cobalt system multiple oxide or a lithium manganese system multiple oxideAlthough it is conductive polymer compoundssuch as polypyrrolepoly anilinepoly para-phenylenepolyacethyleneand poly acene system materiala pseudo-graphite structure carbonaceous materialetc.it is not limited to these.
[0017]As negative electrode active material used for a compound negative electrode (B_1)the following charges of a battery electrode material are mentioned.
[0018]Namelycarbonaceous materialssuch as carbon[For exampleanalysis result according [the above-mentioned carbonaceous material] to an X diffraction etc.; lattice spacing (d002) -- size [ ] of microcrystal of 3.35 to 3.40A a shaft orientations -- more than La 200A -- size [ ] of microcrystal of c shaft orientations -- more than Lc 200A true density 2.00 to 2.25g / cm^3.Although what is the end of carbon powder (mean particle diameter of 15 micrometers or less) a pitch of anisotropy was calcinated at temperature of not less than 2000 **or carbon fiber is desirableof courseit is not limited to these ranges.]Although it is lithium metal content alloyssuch as a lithium metallithium aluminumlithium leadlithium tinlithium aluminum tinlithium galliumand a Wood metaletc. as a negative electrode (B_2)it is not limited to these.
[0019]About a coating method of a compound anode (A) of this inventionand a compound negative electrode (B_1). For examplealthough it is desirable to apply to arbitrary thickness and arbitrary shape using meanssuch as roller coatingsuch as an applicator rollscreen coatinga doctor blade methodspin coatingand a bar coderit is not limited to these. When these means are usedit is possible to make real surface area of an electroactive substance in contact with an electrolyte layer and a current collector increase.
[0020]Necessity is accepted in these cases and it is carbon (with carbon here.)such as

graphitecarbon blackand acetylene black. It has the completely different characteristic from carbon in above-mentioned negative electrode active material. And electrical conducting materialssuch as metal powder and conductive metallic oxidecan be mixed in a compound anode (A) and a compound negative electrode (B_1)and improvement in electronic conduction can be aimed at.

[0021]When manufacturing the above-mentioned compound anode (A) and a compound negative electrode (B_1)in order to obtain a uniform mixture dispersion systemseveral sorts of dispersing agents and carrier fluid can be added. It is also possible to add a thickeneran extenderan adhesion adjuvantetc. furthermore.

[0022]

[Example]Hereafteralthough an example explains the details of this inventionthis invention is not limited to these.

(Example 1) According to the following procedurethe sheet-shaped cell of the example 1 of an experiment was produced.

a) Use manganese dioxide as positive active material of a celland acetylene black is used as a conducting agentAnd what mixed the organic compound which mixed polyethylene-glycol diacrylate (molecular weight: 5000) and polyethylene-glycol monoacrylate (molecular weight: 400) to the wt. ratio of 6:4 was used as a compound anode.

[0023]The manufacturing method of this compound anode is as follows. To namelythe thing which mixed vanadium pentoxide and acetylene black with the wt. ratio of 85:15. To the organic compound 10 above-mentioned weight sectionlithium perchlorate 1 weight sectionWhat mixed propylene carbonate 20 weight section and Palladium on 4-to 8-mesh carbon(Palladium content 1.0%) (made by Aldrich)0.2 weight sectionIt mixed with the wt. ratio of 10:3 among a dry inert gas atmosphere. The cast was carried out on the charge collector in which the conductive carbon tunic was formed on the surface of the anode current collector which consists these mixtures of stainless steel. Thenthe above-mentioned compound anode was stiffened among a dry inert gas atmosphere by irradiating with the electron beam of amount of electron beams 10Mrad. The thickness of the compound anode tunic formed on the positive pole collector was 60 micrometers.

[0024]b) This was stuck by pressure on the negative-electrode collecting electrode plate which consists of stainless steelusing a lithium metal as negative electrode active material of a cell.

[0025]Nextin order to make the ion-conductive high molecular compound layer of this invention form on the above-mentioned lithium metal. Organic compound 30 weight section and lithium perchlorate 6 weight section which mixed polyethylene-glycol diacrylate (molecular weight 5000) and polyethylene-glycol monoacrylate (molecular weight 400) to 6:4The cast of what mixed propylene carbonate 64 weight section was carried out on the above-mentioned lithium metaland the electron beam of amount of electron beams 8Mrad was irradiated with and stiffened among an inert gas atmosphere. The thickness of the electrolyte layer obtained by this was 20 micrometers.

[0026]c) The sheet-shaped cell was producedrespectively by contacting the electrolyte / lithium / negative pole collector obtained by band the positive pole collector / compound anode obtained by a.

[0027]Drawing 1 is a sectional view of the sheet-shaped cell of this invention. One in a figure is an anode current collector which consists of stainless steeland serves also as the exterior. 2 was a compound anodeand acetylene black was used as a conducting agent

and it used the ion-conductive high molecular compound of this invention for positive active material for manganese dioxide as a binder. 3 is an electrolyte layer which consists of an ion-conductive high molecular compound of this invention. 4 is metal lithiumand 5 is a negative-electrode collecting electrode plate which consists of stainless steeland serves also as the exterior. 6 is an obturation agent which consists of denaturation polypropylene.

[0028](Comparative example) In the compound anode of an examplePalladium on 4-to 8-mesh carbon is not included in a compound anodeand also it is the same manufacturing method as the sheet-shaped cell of an exampleand the cellular structureand the sheet-shaped cell of the comparative example was produced.

[0029]Although the electrode area of the sheet-shaped cell of this example 1 and the comparative example 1 can be variously changed according to a making processit produced what made the electrode area 100 cm^2 in this example 1 and the comparative example 1.

[0030](Experiment 1) The initial discharge characteristic when it discharges by 25 **0.1mA/cm^2 of the sheet-shaped cell of this example 1 and the comparative example 1and the discharge characteristic after 60 ** 100-day preservation were investigated. Drawing 2 shows the discharge characteristic (initial discharge characteristic) immediately after cell productionand the discharge characteristic after 60 ** 100-day preservation. It is admitted that the sheet-shaped cell of Example 1 of this invention is excellent in an initial discharge characteristic and the discharge characteristic after 60 ** 100-day preservation as compared with the sheet-shaped cell of the comparative example 1 so that clearly from drawing 2. Since bulging by the generation of gas mentioned later does not exist by the sheet-shaped cell of this example as this causeit is possible that contact of a compound anode / electrolyte layerand a negative electrode/electrolyte layer is good.

[0031](Experiment 2) The number of the sheet-shaped cells which blistered [60 **] after preservation on the 100th was investigated using the sheet-shaped cell of this example 1 and the comparative example 1. As shown in Table 1in the sheet-shaped cell of the comparative example 1generating of bulging was checked in 28% of cellbut the result did not check bulging in the cell which added Palladium on 4-to 8-mesh carbon which is a sheet-shaped cell of Example 1 of this invention. Palladium on4-to 8-mesh carbon may be used beforehandsprinkling on manganese dioxide.

[0032]

[0033](Example 2) The sheet-shaped cell of Example 2 was produced according to the following procedure.

a) Use vanadium pentoxide as positive active material of a celland acetylene black is used as a conducting agentAnd what mixed the organic compound which mixed polyethylene-glycol diacrylate (molecular weight: 5000) and polyethylene-glycol monoacrylate (molecular weight: 400) to the wt. ratio of 6:4 was used as a compound anode.

[0034]The manufacturing method of this compound anode is as follows. To namelythe thing which mixed vanadium pentoxide and acetylene black with the wt. ratio of 85:15. the organic compound 10 above-mentioned weight section -- hexafluoride -- arsenic acid -- lithium 1 weight section and ethylene carbonate -- 10 weight sectionWhat mixed 2-

methyltetrahydrofuran 10 weight section and Palladium on4-to 8-mesh carbon(Palladium content 1.0%) (made by Aldrich)0.2 weight section The inside of a dry inert gas atmosphereIt mixed with the wt. ratio of 10:3. The cast was carried out on the charge collector in which the conductive carbon tunic was formed on the surface of the anode current collector which consists these mixtures of stainless steel. Thenthe above-mentioned compound anode was stiffened among a dry inert gas atmosphere by irradiating with the electron beam of amount of electron beams 10Mrad. The thickness of the compound anode tunic formed on the positive pole collector was 60 micrometers.
[0035]b) This was stuck by pressure on the negative-electrode collecting electrode plate which consists of stainless steelusing a lithium metal as negative electrode active material of a cell.
[0036]Nextin order to make the ion-conductive high molecular compound layer of this invention form on the above-mentioned lithium metal. the organic compound 30 above-mentioned weight section and hexafluoride -- arsenic acid -- lithium 6 weight section and ethylene carbonate -- 32 weight sectionAnd the cast of what mixed 2-methyltetrahydrofuran 32 weight section was carried out on the above-mentioned lithium metaland the electron beam of amount of electron beams 8Mrad was irradiated with and stiffened among an inert gas atmosphere. The thickness of the electrolyte layer obtained by this was 20 micrometers.
[0037]c) The sheet-shaped cell was producedrespectively by contacting the electrolyte / lithium / negative pole collector obtained by band the positive pole collector / compound anode obtained by a.
[0038](Comparative example 2) In the compound anode of Example 2Palladium on 4-to 8-mesh carbon is not included in a compound anodeand also it is the same manufacturing method as the sheet-shaped cell of Example 2and the cellular structureand the sheet-shaped cell of the comparative example 2 was produced.
[0039]Although the electrode area of the sheet-shaped cell of this example 2 and the comparative example 2 can be variously changed according to a making processit produced what made the electrode area 100 cm^2 in this example 2 and the comparative example 2.
[0040](Experiment 3) The charge-and-discharge cycle test was done using the sheet-shaped cell of this example 2 and the comparative example 2 immediately after cell production and after 60 ** 100-day preservation. The charge-and-discharge cycle test of 50microA/cm^2 constant current was done at 25 **. The above-mentioned charge-and-discharge cycle test conditions were made into the charge final voltage 3.2V and the discharge final voltage 2.0V. Drawing 3 shows the number of charging and discharging cyclesand the relation of cell capacity. As drawing 3 showsit turns out that the sheet-shaped cell by this invention shows the outstanding charge-discharge cycle characteristic as compared with the sheet-shaped cell of a comparative example. Since bulging by the generation of gas does not exist by the sheet-shaped cell of this example as this causeit is possible that contact of a compound anode / electrolyte layerand a negative electrode/electrolyte layer is good.
[0041](Experiment 4) The number of the sheet-shaped cells which blistered [60 **] after preservation on the 100th was investigated using the sheet-shaped cell of this example 2 and the comparative example 2. As shown in Table 2in the sheet-shaped cell of the comparative example 2generating of bulging was checked in 20% of cellbut the

result did not check bulging in the cell which added Palladium on 4-to 8-mesh carbon which is a sheet-shaped cell of Example 2 of this invention. Palladium on4-to 8-mesh carbon may be used for vanadium pentoxidesprinkling it beforehand.
[0042]

[0043](Example 3) According to the following procedurethe sheet-shaped cell of Example 3 of this invention was produced.
a) Use $LiCoO_2$ as positive active material of a celland acetylene black is used as a conducting agentAnd what mixed polyethylene-glycol diacrylate (molecular weight: 5000) and polyethylene-glycol monoacrylate (molecular weight: 400) with the organic compound mixed with the wt. ratio of 6:4 was used as a compound anode.
[0044]The manufacturing method of this compound anode is as follows. To namelythe thing which mixed $LiCoO_2$ and acetylene black with the wt. ratio of 85:15. To the organic compound 10 above-mentioned weight sectiontetrafluoride lithium borate 1 weight sectionWhat mixed 1 and 2-dimethoxyethane 10 weight sectiongamma-butyrolactone 10 weight sectionand Palladium on 4-to 8-mesh carbon(Palladium content1.0%) (made by Aldrich)0.2 weight sectionIt mixed with the wt. ratio of 10:3 among a dry inert gas atmosphere. The cast was carried out on the charge collector in which the conductive carbon tunic was formed on the surface of the anode current collector which consists these mixtures of aluminum. Thenthe above-mentioned compound anode was stiffened among a dry inert gas atmosphere by irradiating with the electron beam of amount of electron beams 12Mrad. The thickness of the compound anode tunic formed on the positive pole collector was 60 micrometers.
[0045]Nextin order to make an ion-conductive high molecular compound form on the above-mentioned compound anode. What mixed organic compound 30 above-mentioned weight sectiontetrafluoride lithium borate 6 weight section1and 2-dimethoxyethane 32 weight section and gamma-butyrolactone 32 weight sectionThe cast is carried out in a dry inert gas atmosphere and on the above-mentioned compound anodeafter thatamong a dry inert gas atmosphereit irradiated with the electron beam of amount of electron beams 8Mradand the above-mentioned ion-conductive high molecular compound layer was stiffened. The thickness of the electrolyte layer obtained by this was 25 micrometers.
[0046]b) The thing which mixed polyethylene-glycol diacrylate (molecular weight: 5000) and polyethylene-glycol monoacrylate (molecular weight: 400) with the organic compound mixed with the wt. ratio of 6:4 was used as a compound negative electrodeusing carbon powder as negative electrode active material of a cell.
[0047]The manufacturing method of this compound negative electrode is as follows. To carbon powder and the organic compound 10 above-mentioned weight sectionnamelytetrafluoride lithium borate 1 weight sectionWhat mixed 1 and 2-dimethoxyethane 10 weight sectiongamma-butyrolactone 10 weight sectionand Palladium on 4-to 8-mesh carbon(Palladium content 1.0%) (made by Aldrich)0.2 weight sectionIt mixed with the wt. ratio of 8:2 among a dry inert gas atmosphere. The cast of these mixtures was carried out on the negative-electrode collecting electrode plate which consists of stainless steel. Thenthe above-mentioned compound negative electrode was stiffened among a dry inert gas atmosphere by irradiating with the electron beam of amount of electron beams 15Mrad. The thickness of the compound negative electrode

formed on the negative pole collector was 30 micrometers.
[0048]Nextin order to make an ion-conductive high molecular compound form on the above-mentioned compound negative electrode. What mixed organic compound 30 above-mentioned weight sectiontetrafluoride lithium borate 6 weight section1and 2-dimethoxyethane 32 weight section and gamma-butyrolactone 32 weight sectionThe cast is carried out in a dry inert gas atmosphere and on the above-mentioned compound negative electrodeafter thatamong a dry inert gas atmosphereit irradiated with the electron beam of amount of electron beams 8Mradand the above-mentioned ion-conductive high molecular compound layer was stiffened. The thickness of the electrolyte layer obtained by this was 25 micrometers.
[0049]c) The sheet-shaped cell of Example 2 of this invention was produced by contacting the electrolyte layer / compound negative electrode / negative pole collector obtained by band the positive pole collector / compound anode / electrolyte layer obtained by a.
[0050](Comparative example 3) In the compound anode and compound negative electrode of Example 3Palladium on 4-to 8-mesh carbon is not included in a compound anode and a compound negative electrodeand also it is the same manufacturing method as the sheet-shaped cell of Example 3and the cellular structureand the sheet-shaped cell of the comparative example 2 was produced.
[0051]Although the electrode area of the sheet-shaped cell of this example 3 and the comparative example 3 can be variously changed according to a making processit produced what made the electrode area 100 cm^2 in this example 3 and the comparative example 3.
[0052](Experiment 5) The charge-and-discharge cycle test was done at 25 ** using the sheet-shaped cell of this example 3 and the comparative example 3 the charge-and-discharge cycle test of 50microA/cm^2 constant currentand 100 days after 60 **. The above-mentioned charge-and-discharge cycle test was done as the charge final voltage 4.1V and the discharge final voltage 2.7V. Drawing 4 shows the number of charging and discharging cyclesand the relation of cell capacity. As drawing 4 showsit turns out that the sheet-shaped cell by this invention shows the outstanding charge-discharge cycle characteristic as compared with the sheet-shaped cell of a comparative example. Since bulging by the generation of gas does not exist by the sheet-shaped cell of this example as this causeit is possible that contact of a compound anode / electrolyte layerand a compound negative electrode / electrolyte layer is good.
[0053](Experiment 6) The number of the sheet-shaped cells which blistered [60 **] after preservation on the 100th was investigated using the sheet-shaped cell of this example 3 and the comparative example 3. As a resultas shown in Table 3in the sheet-shaped cell of the comparative example 3generating of bulging was checked in 42.5% of cellbut. Bulging was not checked in the cell which added Palladium on 4-to 8-mesh carbon which is a sheet-shaped cell of Example 3 of this invention. Palladium on 4-to 8-mesh carbon may be used for $LiCoO_2$sprinkling it beforehand.
[0054]

[0055](Example 4) It was made the same as an example (1) except arranging Palladium on 4-to 8-mesh carbon on Li surface. (In this casePalladium on 4-to 8-mesh carbon does

not contain in an anode)
[0056](Example 5) It was made the same as an example (1) except having arranged to sandwich shape between the ion-conductive high molecular compound layers which do not contain the ion-conductive high molecular compound layer containing Palladium on 4-to 8-mesh carbon. (In this casePalladium on 4-to 8-mesh carbon does not contain in an anode)
[0057](Example 6) It was made the same as an example (1) except having arranged Palladium on 4-to 8-mesh carbon like (drawing 5) to the edge part in cells other than an electrode and a separator. (In this casePalladium on4-to 8-mesh carbon is not contained in the anode separator) As a result of performing the investigation same about an example (4)(5)and (6) in addition as the experiment 2there was no cell which blistered as shown in Table 1.
[0058](Example 7) Manganese dioxide of positive active material 85 weight sectionsconducting agent acetylene black 7 weight sectionA mixture sheet with a thickness of 0.2 mm which comprises binder Teflon 5 weight section and Palladium on 4-to 8-mesh carbon(Palladium Cont 1.0%)3 weight sectionIt was stuck by pressure on the stainless steel foil which arranged denaturation polypropylene as a sealing agent on the circumferenceand was considered as the anode. Lithium foil about 0.1 mm thick was stuck by pressure on stainless steel foiland it was considered as the negative electrode.
[0059]It carried out being decompression impregnated of the electrolysis solution which comprises IM lithium perchlorate and a propylene carbonate solution at the separator which comprises the above-mentioned anode and a polypropylene HIREN nonwoven fabric. The anodethe separatorand the negative electrode were laminatedthe sealing agent portion of the circumference of the above was heat sealedand the cell was completed.
[0060](Example 7 of proportionality) It was made the same as Example 7 except having made the mixture ratio of positive electrode mixture into manganese dioxide 85 weight-section acetylene black 10 weight section and Teflon 5 weight.
[0061](Experiment) The neglect test 60 ** for 100 days was presented with the cell of this example and a comparative example. In the examplebulging was not generated to 10 cell bulging having occurred in the comparative example in 25 cells.
[0062](Example 8) Cobalt-acid-lithium 85 weight-section acetylene black 7 weight section of positive active materialThe mixture sheet with a thickness of 0.2 mm which comprises Teflon 5 weight-section Palladium on 4-to 8-mesh carbon3 weight section was stuck by pressure on the aluminium foil which arranged denaturation propylene as a sealing agent on the circumferenceand it was considered as the anode. The mixture sheet with a thickness of 0.2 mm which comprises carbon powder 95 weight section and Teflon 5 weight section was stuck by pressure on nickel foiland it was considered as the negative electrode. It carried out being decompression impregnated of the electrolysis solution which comprises IM lithium-hexafluorophosphate ethylene carbon NEITO solution at the separator which comprises an anodea negative electrodeand a polypropylene micropore film. The anodethe separatorand the negative electrode were laminatedthe above-mentioned circumference sealing agent portion was heat sealedand the cell was completed.
[0063](Comparative example 8) It was presupposed except having made the mixture ratio of positive electrode mixture into cobalt-acid-lithium 85 weight sectionacetylene black 10 weight sectionand Teflon 5 weight section that it is the same as Example 8.

[0064](Example 9) It was presupposed except having made the mixture ratio of negative electrode mixture into carbon powder 92 weight sectionTeflon 25 weight sectionand Palladium on 4-to 8-mesh carbon3 weight section that it is the same as the comparative example 8.
[0065](Experiment) The charging and discharging cycle test was presented with the cell of Examples 8 and 9 and the comparative example 8 immediately after and after 60 ** the neglect during 100 days. Charging and discharging cycle tests are test temperature the current density of 0.5 mA of 25 ** /and $cm^2$and were made into the charge final voltage 4.1V and the discharge final voltage 2.7V. Drawing 6 shows the result of a charging and discharging cycle test. The cell of Examples 8 and 9 has the small fall of the capacity accompanying the cycle progress of an immediately after so that clearly from drawing 6Compared with the thing in which the fall of capacity is [the capacity after 60 ** neglect] small compared with the next capacitythe capacity lowering accompanying progress of a cycle and the capacity lowering after 60 ** 100-day neglect were size in the cell of the comparative example 8.
[0066]In the next cellthe cycle progressed to the cell of the comparative example 8 to bulging not having occurred in the cell of Examples 8 and 9 in Tessand bulging occurred in ** after preservation. In the cell of the comparative example 8the internal impedance of a cell increases by generating of bulgingand it is thought that capacity lowering arose.
[0067]
[Effect of the Invention]This invention has very high workability as above-mentionedand provides a cell with high long term reliability and safety.
Being able to provide the small lightweight sheet-shaped cell which has high performance and high energy densitythe industrial value is size.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]It is a sectional view of the sheet-shaped cell of this invention.
[Drawing 2]The initial discharge characteristic of the sheet-shaped cell of Example 1 and the comparative example 1 and the discharge characteristic after 60 ** 100-day preservation are shown.
[Drawing 3]It is the graph which showed the number of charging and discharging cycles of the sheet-shaped cell of Example 2 and the comparative example 2and the relation of cell capacity.
[Drawing 4]It is the graph which showed the number of charging and discharging cycles of the sheet-shaped cell of Example 3 and the comparative example 3and the relation of cell capacity.
[Drawing 5]It is a sectional view of the sheet-shaped cell of this invention.
[Drawing 6]It is the graph which showed the number of charging and discharging cycles of Examples 8 and 9and the relation of cell capacity.
[Description of Notations]
1 Positive pole collector
2 Compound anode

3 Separator
4 Metal lithium or a compound negative electrode
5 Negative pole collector
6 Obturation agent
7 Gas absorbent